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## Viscoelastic Surfactant Fluids Stable at High Brine Concentrations

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### Technical Field of the Invention

This invention relates to the drilling, completion, and stimulation of hydrocarbon wells and in particular to fluids and methods for hydraulic fracturing, gravel packing, or drilling in a subterranean formation.

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### Background of the Invention

Hydrocarbons (oil, natural gas, etc.) are obtained from a subterranean geologic formation (i.e., a "reservoir") by drilling a well that penetrates the hydrocarbon-bearing formation. This provides a partial flowpath for the hydrocarbon to reach the surface. In order for the hydrocarbon to be "produced," that is travel from the formation to the wellbore (and ultimately to the surface), there must be a sufficiently unimpeded flowpath from the formation to the wellbore. This flowpath is through the formation rock—e.g., sandstone, carbonates—which has pores of sufficient size, connectivity, and number to provide a conduit for the hydrocarbon to move through the formation.

Viscous fluids play many important roles in oilfield service applications. The viscosity of the fluids allows them to carry particles from one region of the formation, the wellbore, or the surface equipment to another. For example, one role of a viscous fluid is as a drilling fluid, which is injected into the wellbore during drilling to lubricate the drilling bit and carry drilled cuttings from around the drilling bit out of the wellbore to the surface.

After the well is drilled, if the formation has relatively high permeability, the production of sand grains from the formation (which contaminate the produced hydrocarbon and erode equipment) can be minimized by the placing of a gravel pack and/or screen around

the perimeter of the wellbore in the production zone. Viscous fluids are used to carry the gravel into position to form the gravel pack.

Alternatively, if the formation has relatively low permeability, either naturally or through the addition of other fluids, the formation of scales, or other processes, the formation can be fractured to increase the permeability. Fracturing involves literally breaking a portion of the surrounding strata, by injecting a specialized fluid into the wellbore directed at the face of the geologic formation at pressures sufficient to initiate and extend a fracture in the formation (i.e. above the minimum in situ rock stress). More particularly, a fluid is injected through a wellbore, and then the fluid exits the wellbore and is directed against the face of the formation at a pressure and flow rate sufficient to overcome the minimum in situ stress (also known as minimum principal stress) to initiate and/or extend a fracture(s) into the formation. Typically, the fluid comprises a proppant, such as glass beads, sand, etc., that lodges in the fracture(s) during injection, and holds the fracture(s) open after the pressure is released. The viscous fluid carries the proppant into the fracture(s).

The most common way in which these fluids are rendered viscous is by inclusion of polymers. Exemplary polymers include solvatable polysaccharides, e.g., galactomannan gums, glycomannan gums, and cellulose derivatives. However, polymers pose a number of drawbacks inherent in their use. First, coating of dehydrated polymer on the formation can lead to reduced permeability. Second, fluids comprising the polymers often have a high friction pressure.

The use of viscoelastic surfactants (VES) to render a fluid viscous has also been seen. A VES is a molecule with both hydrophobic and hydrophilic portions, and is capable of forming micelles that are sheet-like, spherical, vesicular, or worm-like. Fluids comprising VES have a number of advantages over polymer-based fluids. A chief advantage lies in fracturing applications; upon contact with a hydrocarbon in the formation, the VES are generally soluble in the hydrocarbon and leave little, if any, residual VES in the proppant pack.

However, fluids comprising VES tend to lose viscosity at high brine concentration ( $\geq 10$  lb/gal). As a result, VES-based fluids have seen little use as gravel-packing fluids or drilling fluids, or in other applications requiring heavy fluids to balance well pressure. Therefore, it is desirable to have VES-based fluids that can substantially retain viscosity at high brine concentrations, and thus be useful in gravel pack fluid or drilling fluid applications.

Summary of the Invention

The present invention relates to the use of VES-based fluids which substantially retain viscosity at high brine concentrations. One embodiment of the invention is a well treatment fluid composition that comprises a VES; and a high brine carrier fluid, i.e. a carrier fluid comprising an inorganic salt and having a density of at least 10 lb/gal. Optionally, the well treatment fluid may comprise a cosurfactant.

A "viscoelastic surfactant" or "VES" is a molecule with both hydrophobic and hydrophilic portions, and is capable of forming micelles that are sheet-like, spherical, vesicular, or worm-like, preferably worm-like. Preferably, the VES has either a saturated or unsaturated alkyl ( $C_{\leq 22}$ ) chain hydrophobic portion, or a non-ionic or zwitterionic hydrophilic portion, or both. A more preferred viscoelastic surfactant comprises a betaine moiety and an oleic acid moiety, such as the surfactant in BET-O-30 (Rhodia).

Other VES, which may be employed either alone or in combination, include erucyl bis(2-hydroxyethyl) methyl ammonium chloride; erucyl trimethyl ammonium chloride; N-methyl-N,N-bis(2-hydroxyethyl) rapeseed ammonium chloride; oleyl methyl bis(hydroxyethyl) ammonium chloride; octadecyl methyl bis(hydroxyethyl) ammonium bromide; octadecyl tris(hydroxyethyl) ammonium bromide; octadecyl dimethyl hydroxyethyl ammonium bromide; cetyl dimethyl hydroxyethyl ammonium bromide; cetyl methyl bis(hydroxyethyl) ammonium salicylate; cetyl methyl bis(hydroxyethyl) ammonium 3,4,-dichlorobenzoate; cetyl tris(hydroxyethyl) ammonium iodide; bis(hydroxyethyl) soya amine; N-methyl, N-hydroxyethyl tallow amine; bis(hydroxyethyl) octadecyl amine; cosyl dimethyl hydroxyethyl ammonium bromide; cosyl methyl bis(hydroxyethyl) ammonium chloride; cosyl tris(hydroxyethyl) ammonium bromide; dicosyl dimethyl hydroxyethyl ammonium bromide; dicosyl methyl bis(hydroxyethyl) ammonium chloride; dicosyl tris(hydroxyethyl) ammonium bromide; hexadecyl ethyl bis(hydroxyethyl) ammonium chloride; hexadecyl isopropyl bis(hydroxyethyl) ammonium iodide; N,N-dihydroxypropyl hexadecyl amine, N-methyl, N-hydroxyethyl hexadecyl amine; N,N-dihydroxyethyl dihydroxypropyl oleyl amine; N,N-dihydroxypropyl soya amine; N,N-dihydroxypropyl tallow amine; N-butyl hexadecyl amine; N-hydroxyethyl octadecyl amine; N-hydroxyethyl cosyl amine; cetyl amino, N-octadecyl pyridinium chloride; N-soya-N-ethyl morpholinium ethosulfate; methyl-1-oleyl amido ethyl-2-oleyl imidazolinium-methyl sulfate; and methyl-1-tallow amido ethyl-2-tallow imidazolinium-methyl sulfate.

The concentration of the VES in the solution is preferably between about 1 wt% and about 10 wt%. More preferably, the concentration is about 2.9 wt% to about 5 wt%.

The optional cosurfactant may be used to increase the gel strength and reduce the shear sensitivity of the VES-based fluid, if desired. A preferred cosurfactant is sodium dodecabenzenesulfonate (SDBS). The concentration of the cosurfactant in the fluid is preferably about 0.1 wt% to about 1 wt%. More preferably, the concentration of the cosurfactant in the fluid is about 0.29 wt% to about 0.5 wt%.

The carrier fluid is a brine, i.e. water comprising an inorganic salt. Preferred inorganic salts include calcium halides, more preferably calcium chloride or calcium bromide.

Zinc halides, especially zinc bromide, are not preferred, as it has been observed that this salt tends to reduce the viscosity of the VES-based solution.

The concentration of the inorganic salt in the fluid is at least high enough to bring the density of the carrier fluid to at least about 10 lb/gal, and preferably from about 10 lb/gal to about 15 lb/gal. The inorganic salt can be added to the carrier fluid in any hydration state (i.e. anhydrous, monohydrated, dihydrated, etc.).

Other components can be included in the fluid, depending on its intended use. If the fluid is to be used as a drilling fluid, it preferably comprises emulsifiers and other surface active agents, viscosifiers such as organoclays and polymers, filtration control agents such as Gilsonite and organically modified lignite, density increasing agents such as powdered barytes or hematite or calcium carbonate, or other wellbore fluid additives known to those skilled in the art.

If the fluid is to be used as a gravel packing fluid, it preferably comprises gravel. Other additives that can be used in a gravel packing fluid include corrosion inhibitors, scale inhibitors, biocides, or leak-off agents, among others.

If the fluid is to be used as a fracturing fluid, it preferably comprises a proppant, such as glass beads, sand, or others known in the art. It can also comprise a proppant flowback inhibitor.

The composition can optionally further comprise one or more additives, such as scale inhibitors or biocides, depending on the intended use, formation conditions, and other parameters readily apparent to one of ordinary skill in the art.

Another aspect of the present invention is a method of drilling a wellbore. The method includes the step of injecting a VES-based fluid composition into a wellbore at a flow

rate and pressure sufficient to lubricate the drilling bit and carry cuttings to the surface. The composition comprises a VES and a high brine carrier fluid, as mentioned above.

Yet another aspect of the present invention is a method of hydraulically fracturing a subterranean formation. The method includes the step of injecting a VES-based fluid composition via a wellbore into a subterranean formation at a flow rate and pressure sufficient to produce or extend a fracture in the formation. The composition comprises a VES, a high brine carrier fluid, and a proppant, as mentioned above.

Still another aspect of the present invention is a method of emplacing a gravel pack in a wellbore. The method includes the step of injecting a VES-based fluid composition into a wellbore at a flow rate and pressure sufficient to emplace a gravel pack in the wellbore. The composition comprises a VES, a high brine carrier fluid, and the gravel, as mentioned above. Preferably, the method is performed in formations having a temperature less than about 260°F.

The compositions and methods of the present invention provide several substantial advantages over prior fluids and methods. Though not to be bound by theory, it is believed that the cosurfactant functions to allow the VES to substantially retain its viscosity in the presence of high inorganic salt concentrations. The present invention also is relatively simple and inexpensive to manufacture.

#### Brief Description of the Drawings

Figure 1 shows viscosity as a function of temperature for test solutions of a fluid comprising 10% BET-O-30 (29% betaine-oleic acid VES, 17% propylene glycol, 48.5% water; Rhodia) with 0.3% SDBS in aqueous solution with 48%  $\text{CaCl}_2$  (diamonds) and 80%  $\text{CaCl}_2$  (squares).

Figure 2 shows viscosity as a function of temperature for test solutions of a fluid comprising 10% BET-O-30 (29% betaine-oleic acid VES, 17% propylene glycol, 48.5% water; Rhodia) with 0.3% SDBS in aqueous solution with 60%  $\text{CaBr}_2$  (diamonds) and 100%  $\text{CaBr}_2$  (squares).

#### Detailed Description of Preferred Embodiments

##### Components of the Fluid

While the compositions of the present invention are described herein as comprising certain materials, it should be understood that the composition can optionally comprise two or

more chemically different such materials. For example, a composition could comprise a mixture of two or more viscoelastic surfactants. Two or more of any of the other components could also be present in the composition.

5 A fluid of the present invention comprises a "viscoelastic surfactant" or "VES." The VES is a molecule with both hydrophobic and hydrophilic portions, and is capable of forming micelles that are sheet-like, spherical, vesicular, or worm-like, preferably worm-like. Preferably, the VES has either a saturated or unsaturated alkyl (C<sub>22</sub>) chain hydrophobic portion, or a non-ionic or zwitterionic hydrophilic portion, or both. A more preferred viscoelastic surfactant comprises a betaine moiety and an oleic acid moiety, such as the active  
10 ingredient in BET-O-30 (Rhodia). It should be noted that the oleic acid stock from which the oleic acid moiety is derived is generally about 75% pure to about 85% pure, and the balance of the stock comprises other fatty acids, such as linolic acid, linoleic acid, etc. Some of these other fatty acids may be present in about 15% to about 25% of the molecules of the VES in place of the oleic acid.

15 Other VES, which may be employed either alone or in combination, include erucyl bis(2-hydroxyethyl) methyl ammonium chloride; erucyl trimethyl ammonium chloride; N-methyl-N,N-bis(2-hydroxyethyl) rapeseed ammonium chloride; oleyl methyl bis(hydroxyethyl) ammonium chloride; octadecyl methyl bis(hydroxyethyl) ammonium bromide; octadecyl tris(hydroxyethyl) ammonium bromide; octadecyl dimethyl hydroxyethyl  
20 ammonium bromide; cetyl dimethyl hydroxyethyl ammonium bromide; cetyl methyl bis(hydroxyethyl) ammonium salicylate; cetyl methyl bis(hydroxyethyl) ammonium 3,4,-dichlorobenzoate; cetyl tris(hydroxyethyl) ammonium iodide; bis(hydroxyethyl) soya amine; N-methyl, N-hydroxyethyl tallow amine; bis(hydroxyethyl) octadecyl amine; cosyl dimethyl hydroxyethyl ammonium bromide; cosyl methyl bis(hydroxyethyl) ammonium chloride;  
25 cosyl tris(hydroxyethyl) ammonium bromide; dicosyl dimethyl hydroxyethyl ammonium bromide; dicosyl methyl bis(hydroxyethyl) ammonium chloride; dicosyl tris(hydroxyethyl) ammonium bromide; hexadecyl ethyl bis(hydroxyethyl) ammonium chloride; hexadecyl isopropyl bis(hydroxyethyl) ammonium iodide; N,N-dihydroxypropyl hexadecyl amine, N-methyl, N-hydroxyethyl hexadecyl amine; N,N-dihydroxyethyl dihydroxypropyl oleyl amine;  
30 N,N-dihydroxypropyl soya amine; N,N-dihydroxypropyl tallow amine; N-butyl hexadecyl amine; N-hydroxyethyl octadecyl amine; N-hydroxyethyl cosyl amine; cetylamino, N-octadecyl pyridinium chloride; N-soya-N-ethyl morpholinium ethosulfate; methyl-1-oleyl

amido ethyl-2-oleyl imidazolinium-methyl sulfate; and methyl-1-tallow amido ethyl-2-tallow imidazolinium-methyl sulfate.

The concentration of the VES in the solution is preferably between about 1 wt% and about 10 wt%. More preferably, the concentration is about 2.9 wt% to about 5 wt%.

5       The optional cosurfactant may be used to increase the gel strength and reduce the shear sensitivity of the VES-based fluid, if desired. A preferred cosurfactant is sodium dodecabenzenesulfonate (SDBS). The concentration of the cosurfactant in the fluid is preferably about 0.1 wt% to about 1 wt%. More preferably, the concentration of the cosurfactant in the fluid is about 0.29 wt% to about 0.5 wt%.

10       Also, a fluid of the present invention comprises a carrier fluid, specifically, a brine. The brine is an aqueous solution comprising an inorganic salt, preferably an alkaline earth inorganic salt, more preferably a calcium halide. Calcium chloride and calcium bromide are especially preferred. Zinc bromide has been found to be unsuitable for use in the fluids of the present invention.

15       The concentration of the inorganic salt in the fluid is at least high enough to bring the density of the carrier fluid to at least about 10 lb/gal, and preferably from about 10 lb/gal to about 15 lb/gal. The inorganic salt can be added to the carrier fluid in any hydration state (i.e. anhydrous, monohydrated, dihydrated, etc.).

20       Optionally, the fluid may comprise further components. Further components of the fluid will vary depending on the fluid's intended use.

      If intended as a drilling fluid, the drilling fluid optionally further comprises any of the following: emulsifiers and other surface active agents, viscosifiers such as organoclays and polymers, filtration control agents such as Gilsonite and organically modified lignite, density increasing agents such as powdered barytes or hematite or calcium carbonate, or other  
25       wellbore fluid additives known to those skilled in the art.

      If intended as a fracturing fluid, the fracturing fluid further comprises a proppant. Suitable proppants include, but are not limited to, sand, bauxite, glass beads, and ceramic beads. If sand is used, it will typically be from about 20 to about 100 U.S. Standard Mesh in size. Mixtures of suitable proppants can be used. Optionally, the proppant or proppants can  
30       be coated with a resin to allow consolidation of the proppant particles into a mass. The concentration of proppant in the fracturing fluid can be any concentration known in the art, and will typically be in the range of about 0.5 to about 20 ppa (pounds of proppant added) per gallon of clean fluid.

The fluid will also typically comprise a proppant. Suitable materials from which the proppant can be made include sand (e.g. 20-40 mesh), bauxite, man-made intermediate-strength or high strength materials, and glass beads. Optionally the proppant can be coated with resin of a type and in an amount that will permit consolidation of the proppant particles into a mass, for example when subjected to the elevated temperatures and pressures of the formation.

The fracturing fluid can also comprise a breaker. The purpose of this component is to "break" or diminish the viscosity of the fracturing fluid so that this fluid is more easily recovered from the fracture during clean-up. Exemplary breakers include oxidizers such as ammonium persulfate. Additionally, the breaker can be encapsulated to delay its release, for example as described in U.S. Pat. No. 4,741,401, which is incorporated herein by reference.

Optionally, the fracturing fluid can further contain one or more additives such as surfactants, breaker aids, salts (e.g., potassium chloride), anti-foam agents, scale inhibitors, and bactericides. Also optionally, the fracturing fluid can contain materials designed to limit proppant flowback after the fracturing operation is complete by forming a porous pack in the fracture zone. Such materials, herein "proppant flowback inhibitors," can be any known in the art, such as are available from Schlumberger under the trade name Propnet™.

If intended as a gravel packing fluid, the fracturing fluid further comprises gravel or sand having a mesh size between 10 and 60 U.S. Standard Sieve Series mesh. The fluid can also comprise corrosion inhibitors, scale inhibitors, biocides, or leak-off agents, among others.

Regardless of the intended use, the fluid can be prepared at any time prior to use by combining the VES, the cosurfactant, and the high brine carrier fluid, as well as any further components. The VES typically can be provided in an aqueous solution, but also can be provided in any other form. The high brine carrier fluid can be prepared by the addition of the inorganic salt to the carrier fluid any time before, during, or after addition of the VES to the fluid.

Additives to be included in the fluid can be added to the fluid at any time prior to use. Additives which can perform their desired function after injection of the fluid can also be added to the fluid after it has been injected into the wellbore.

In another embodiment, the present invention relates to a method of hydraulically fracturing a subterranean formation. Techniques for hydraulically fracturing a subterranean



formation will be known to persons of ordinary skill in the art, and will involve pumping the fracturing fluid into the borehole and out into the surrounding formation. The fluid pressure is above the minimum *in situ* rock stress, thus creating or extending fractures in the formation. See *Stimulation Engineering Handbook*, John W. Ely, Pennwell Publishing Co.,  
5 Tulsa, Oklahoma (1994).

In yet another embodiment, the present invention relates to a method of drilling a wellbore. The method comprises providing a wellbore completion fluid as described above, injecting the fluid into a nascent wellbore in which is acting a drilling bit, and removing cuttings from around the drilling bit with the wellbore completion fluid.

10 In still another embodiment, the present invention relates to a method of gravel packing a wellbore. Gravel packing is typically only used on unconsolidated formations, which tend to produce an undesirably high level of particulates with the hydrocarbon. The method involves the placement of a solution comprising a quantity of gravel and/or sand having a mesh size between 10 and 60 U.S. Standard Sieve Series mesh into the formation  
15 adjacent to the wellbore. It is sometimes desirable to bind the gravel particles together to form a porous matrix for passage of formation fluids while facilitating the filtering out and retainment in the well of the bulk of the unconsolidated sand and/or fines transported to the near wellbore area by the formation fluids. The gravel particles can constitute a resin-coated gravel which is either pre-cured or can be cured by an overflush of a chemical binding agent  
20 once the gravel is in place. In some instances, various binding agents have been applied to the gravel particles to bind them together, forming a porous matrix.

The gravel or sand is placed in the formation adjacent to the wellbore by injecting a fluid comprising a VES, a cosurfactant, a high brine carrier fluid, and the gravel or sand into the wellbore. Optionally, the VES, the cosurfactant, and the high brine carrier fluid are then  
25 removed from the emplaced gravel or sand.

The invention can be better understood by reference to the Examples provided below.

### Examples

#### 30 Example 1

Fluids were prepared comprising 10% BET-O-30 (29% betaine-oleic acid VES, 17% propylene glycol, 48.5% water; Rhodia) with 0.3% SDBS in aqueous solution. The concentration of betaine-oleic acid VES was thus 2.9%. Brines ( $\text{CaCl}_2$ ,  $\text{CaBr}_2$ , or  $\text{ZnBr}_2$ )

were added thereafter, at various test concentrations (w/v %). Because of possible hydration, the test concentrations of the inorganic salts on the anhydrous basis were not exactly determined. Instead, the salt concentrations on the anhydrous basis were quantified from the densities of the fluids as measured at room temperature. Fluid viscosity was recorded using a  
5 Fann 50 cylindrical rotational viscometer.

It was observed that  $\text{ZnBr}_2$  had an immediate negative effect on fluid viscosity. Therefore,  $\text{CaCl}_2$  and  $\text{CaBr}_2$  were examined further.

Figure 1 shows viscosity as a function of temperature for test solutions of the above fluid with 48%  $\text{CaCl}_2$  (diamonds) and 80%  $\text{CaCl}_2$  (10.74 lb/gal) (squares). In contrast to  
10 what would be expected for typical VES-based fluids in the presence of brine, the viscosity of the test solution comprising 80%  $\text{CaCl}_2$  was roughly 2- to 3-fold higher than the viscosity of the test solution with lower  $[\text{CaCl}_2]$  at temperatures greater than about 120°F up to about 260°F.

Figure 2 shows viscosity as a function of temperature for test solutions of the above  
15 fluid with 60%  $\text{CaBr}_2$  (11.50 lb/gal) (diamonds) and 100%  $\text{CaBr}_2$  (12.98 lb/gal) (squares). The viscosity of both samples had a roughly constant viscosity of about 130 cp at 100 s<sup>-1</sup> at temperatures up to about 220°F.

Also, to investigate whether the test solution would undergo phase separation at very high brine concentrations, the test solution was prepared with 160%  $\text{CaBr}_2$  [ $\rho = 1.79 \text{ g/cm}^3$  at  
20 room temperature, 14.94 lb/gal]. The solution was agitated, and then agitation was removed. The resulting mixture showed no phase separation after about 2-3 days at room temperature, although the viscosity of the solution was relatively low.

Therefore, it is possible to generate solutions comprising viscoelastic surfactants which remain at least somewhat viscous at high brine concentrations.

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The preceding description of specific embodiments of the present invention is not intended to be a complete list of every possible embodiment of the invention. Persons skilled in this field will recognize that modifications can be made to the specific embodiments described here that would be within the scope of the present invention.

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